

PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

Complex Esters

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, all British do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of complex esters.

Complex esters are used as lubricants especially as aviation lubricants, and it is important that they should have load carrying properties and show stability against oxidation at relatively high temperatures. Hitherto these desirable properties have been achieved by the use of hindered acids and/or glycols in the preparation of the ester. It has now been found that by ensuring the presence of certain phosphates during the esterification reaction, it is not necessary to use hindered components, or if they are used, the oxidative stability and the load carrying properties of the resulting ester is even greater than if no phosphate had been used.

According to this invention a complex ester is prepared by a process wherein the acidic and alcoholic reactants are reacted together in the presence of an ester or a salt of a phosphorus-containing acid (hereinafter referred to as phosphorus-containing compound). As used in this Specification the term "complex ester" means an ester derived from the reaction of at least three different compounds, each compound having at least one carboxylic or hydroxyl group, wherein at least one of said three different compounds con-

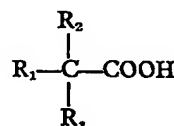
tains two or more carboxyl groups, and another of said three different compounds contains two or more hydroxyl groups.

Suitable compounds from which the complex esters are derived include mono- and polycarboxylic acids or ether acids; monohydric and polyhydric alcohols, and polyol ethers. Examples of such compounds are as follows:

Monocarboxylic acids:

Straight-chains acids such as n-butanoic acid, caproic acid, caprylic acid, pelargonic acid, capric acid, and other acids having between for example 2 and 20 carbon atoms per molecule.

Branched chain acids of the general formula:

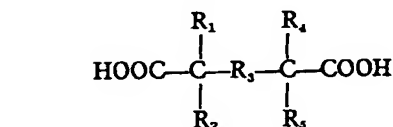


wherein R_1 , R_2 and R_3 are similar of dissimilar hydrocarbyl, (especially alkyl) groups or hydrogen atoms provided that not all three groups are hydrogen atoms. Such acids include α,α dimethyl valeric acid, α,α dimethyl capric acid, α,α dimethyl octanoic acid and many other acids having between for example 4 and 40 carbon atoms per molecule.

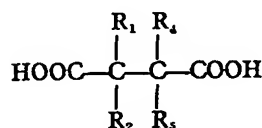
Dicarboxylic acids:

These include straight chain aliphatic or aromatic acids for example, succinic acid, adipic, pimelic acid, azelaic acid, sebacic acid and many other acids having between for example 2 and 20 carbon atoms per molecule.

Also suitable are branched chain dicarboxylic acids of the general formulae



and



where R_3 is an alkylene or hydrocarbyl substituted alkylene group, and R_1 , R_2 , R_4 and R_5 are similar dissimilar hydrocarbyl groups (especially alkyl groups) or hydrogen atoms provided that not all four groups are hydrogen atoms. Examples of branched-chain dicarboxylic acids are tetra alkyl substituted adipic, pimelic, azelaic and sebacic acids wherein the alkyl groups are methyl, ethyl, isopropyl or butyl groups, for instance $\alpha, \alpha, \alpha', \alpha'$, tetra methyl azelaic acid or $\alpha, \alpha, \alpha', \alpha'$ tetramethyl pimelic acid and many other acids containing for example between 6 and 60 atoms per molecule.

Polycarboxylic acids:

Acids having three or more carboxylic acids, e.g. propane tricarboxylic acid, may be used if desired but they are not the preferred acids.

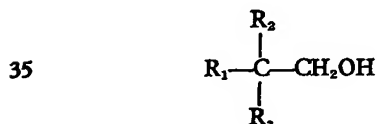
Ether-acids

Methyl, ethyl, and butyl ethers of glycolic acid or diglycolic acid or ethylene diglycolic acid; or the ethyl and butyl ethers of 2-hydroxy-ethoxy-acetic acids.

Monohydric Alcohols

These include straight-chain alcohols, for example, n-hexanol, n-dodecanol, and other monohydric alcohols having for example 1 to 20 carbon atoms per molecule.

Branched chain monohydric alcohols include those of the general formula



wherein R_1 , R_2 , and R_3 are hydrocarbyl (especially alkyl) groups or H atoms provided that they cannot all be H atoms.

Examples of branched chain monohydric alcohols are 2,2,4, - trimethyl pentan - 1 - ol; 2,2 dimethyl hexan 1 - ol; 2,2 dimethyl octan - 1 - ol; 1 methyl cyclohexyl methan - 1 - ol, and many others containing for example between 3 and 40 carbon atoms per molecule.

Glycols

Straight-chain glycols, such as ethylene glycol, propylene glycol and hexylene glycol or the polyethylene or polypropylene glycols of

molecular weight between 150 and 250 may be used.

It is preferable however if branched chain glycols be used, for example those containing between 3 and 40 carbon atoms per molecule, for instance 2,2 - dimethyl propane - 1,3 - diol (i.e. neopentyl glycol); 2 - ethyl 2 - butyl - propane - 1,3 - diol; 2,2 diethyl propane - 1,3 diol; 2 - methyl - 2 - propyl propane - 1,3 - diol.

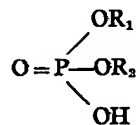
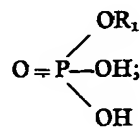
Other polyols

Triols, tetrols or higher polyols may be used, and these include for example trimethylol ethane, trimethylolpropane and pentaerythritol.

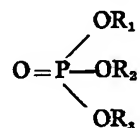
Polyol ethers

Partial ethers of polyols, i.e. ethers having at least one free hydroxyl group, may be used. These include the short chain alkyl ethers of glycols, for example mono-n-butyl ethylene glycol, mono isopropyl hexylene glycol, as well as the mono ethers of polyalkylene glycols, e.g. the mono methyl, ethyl or propyl ethers of polyethylene glycol.

Phosphorus-containing compound may be a salt of a phosphorus-containing acid (e.g. phosphoric acid or phosphorous acid) but is preferably an ester of a phosphorus containing acid. The particularly preferred phosphorus containing compounds are the partial or complete esters of phosphoric acid having the general formulae



and



wherein R_1 , R_2 and R_3 are similar or dissimilar hydrocarbyl groups. Preferably these hydrocarbyl groups contain between 1 and 10 carbon atoms, and preferably the hydrocarbyl groups are alkyl groups, e.g. ethyl, isopropyl, n-butyl, n-hexyl and n-decyl groups. If desired however other hydrocarbyl groups, e.g. aryl groups such as phenyl or cresyl groups, may be present instead of or as well as alkyl groups. The preferred ester is tri-butyl phosphate.

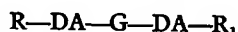
The term "Complex ester" covers a wide range of esters, but it is preferable if the

esters are derived either from the reaction of a compound containing two carboxyl groups, a compound containing two hydroxyl groups, and a compound containing one carboxyl group i.e. an acid-centered complex ester; or from the reaction of a compound containing two hydroxyl groups, a compound containing two carboxyl groups, and a compound containing one hydroxyl group, i.e. a glycol-centered complex ester.

Thus, suitable examples of acid-centered complex esters are those derived from adipic acid, neopentyl glycol and pelargonic acid; sebacic acid, neopentyl glycol and caprylic acid, or sebacic acid, trimethylol propane and caprylic acid. Similarly suitable examples of glycol-centered complex esters are those derived from neopentyl glycol sebacic acid, and 2,2,4, trimethyl pentanol or 2,2' diethyl 1-3 propane diol, azelaic acid and 2,2,4, trimethyl pentanol.

Preferably the complex ester will have a total of between 15 and 80 e.g. between 20 and 65, carbon atoms per molecule.

In preparing the complex esters in accordance with the process of the invention, the reactants are preferably reacted together in substantially stoichiometric proportions according to the ester it is desired to prepare. Thus, for esters of the general formula.



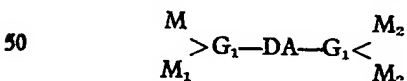
where R and R₁ are residues of similar or dissimilar alcohols or glycol ethers.

DA is the residue of a dicarboxylic acid and G is the residue of a glycol, substantially two moles of dicarboxylic acid per mole of glycol, and per mole of each of the alcohol or glycol ethers are reacted together in one or two stages. Similarly for esters of the general formula



where M and M₁ are residues of similar or dissimilar monocarboxylic acids, and G and DA are as defined above, substantially two moles glycol per mole of dicarboxylic acid, and per mole of each of the monocarboxylic acids are reacted together in one or two stages.

For esters of the general formula



where M₂ and M₁ are residues of similar or dissimilar monocarboxylic acids, G₁ is a triol and M, M₁ and DA are as defined above substantially two moles of triol per mole of dicarboxylic acid and per mole of each of the mono-carboxylic acids are reacted together in one or two stages.

In preparing the complex esters by the

process of the invention all the reactants may be reacted together in one stage, but it is preferable if the reaction is carried out in two stages. In the first stage one reacts the compound forming the centre of the complex ester with the compound which attaches itself directly to the centre-forming compound. In the second stage, the reaction product from the first stage is reacted with the remaining compounds constituting the complex ester. When the reaction is carried out in two stages, the phosphorus containing compound may be used in the first, or the second stage of the reaction, or if desired in both stages of the reaction.

The amount of phosphorus containing compound which need be used in carrying out the process of the invention is preferably quite small, for example less than 5% of the total weight of the reactants. An amount of between 0.5% and 2% of the total weight of the reactants is particularly suitable.

In addition to the use of the phosphorus containing compound, if desired an esterification catalyst, for example paratoluene sulphonic acid or sulphuric acid, may be used. The use of such a catalyst often results in a substantially reduction in reaction time, but the ester is often less thermally stable; hence the use of an esterification catalyst is often not desirable. The amount of catalyst which needs be used is smaller than that of the phosphorus containing compound e.g. between 0.1 and 1.0% of the total weight of the reactants.

In carrying out the esterification reactions by a one stage process one heats the reactants in the presence of phosphorus containing compound, and catalyst (if used) until substantially all the water is removed. The temperature of reaction will depend on the reactants, but will generally be of the order of 150°C, e.g. between 100°C and 200°C. The reaction time will also vary with the reactants, but generally the esterification should be complete in a total of about 10 to 20 hours. The esterification should be carried out under an inert gas atmosphere e.g. with a steady nitrogen bleed.

If the reaction is carried out in two stages, the reaction condition are similar to a one stage process. In the first stage the reaction mixture is heated until substantially all the water is removed, and this will generally take about 4 to 5 hours, from 125°C to 175°C. Preferably one then cools the reaction mixture slightly, e.g. to between 110°C and 140°C before adding further reactant. When the further reactant has been added the reaction mixture is heated until substantially all the water of reaction has been removed. This second stage generally takes about 6 to 15 hours, and the temperature of reaction may be higher than in the first stage, e.g. between about 180°C and 220°C. As with

the single step process the reaction in both stages should be carried out in the presence of an inert atmosphere, e.g. with a steady nitrogen bleed.

- 5 The complex ester is thereafter recovered from the reaction mixture (one or two stage processes) e.g. by stripping under nitrogen. The recovered ester may also be washed, especially with basic inorganic reagents to
10 reduce the acidity of the ester.

- The complex esters prepared in accordance with the process of the invention may be derived from hindered alcohols or hindered carboxylic acids or both. By "hindered alcohol" we mean an alcohol where there are no hydrogen atoms attached to the carbon atom beta to the hydroxyl group, and by a "hindered carboxylic acid" we mean a carboxylic acid where there are no hydrogen atoms attached to the carbon atom alpha to the carboxyl group. If the esters are derived from hindered alcohols or hindered carboxylic acids, such esters will have greater thermal stability than if they are not derived from
25 such alcohols or carboxylic acids.

The invention is now described with reference to the following Examples.

EXAMPLE I

- 30 A complex ester was prepared by a two-stage process. The reactor was charged with 1 mole of adipic acid, 2 moles of neopentyl glycol and 4 gm of tributyl phosphate. The charge melted at about 115°C and the reaction mixture was continuously heated until
35 about 98% to 100% of the theoretical amount

of water was given off. This took about 4 hours with the bulk liquid temperature rising to 150°C. The melting of the reactants was carried out with a nitrogen purge and esterification with a steady nitrogen bleed.

40 After the first stage had been completed, the reaction mixture was cooled to 125° to 130°C and 2.2 moles of pelargonic acid were added, and the reaction was continued to completion. This took another 4 to 5 hours and the reaction mixture temperature rose to 200° to 220°C.

The reaction product was then stripped with a nitrogen bleed to give an ester of 232°C flash point. The ester was then washed with a mixture of sodium carbonate, isopropanol, heptane and water to give a product having a Total Acid No. of not more than 0.10 mg KOH/g. The washed ester was then stripped under nitrogen bleed under conditions of temperature and pressure to give a product having once again a flash point of 232°C. Finally, any residual acidity was reduced by treating the ester with 2% of the weight of ester, of alumina fines, and 2% of the weight of the ester, of animal charcoal and stirring the product for 1 to 1½ hours at 110° to 115°C. The purified ester was obtained by filtration.

EXAMPLE II

65 Using similar reaction techniques to that described in Example I and carrying out the reaction in two stage processes, two further esters were prepared. These esters were subjected to oxidation tests and the results obtained were as follows

Oxidation Resistance of Ester in absence of antioxidants at 228°C.

Ester	Phosphate	After 20 hours		After 50 hours	
		% increase KV 210°F.	Δ tan mg KOH/g	% increase KV 210°C.	Δ tan mg KOH/g
6 mole adipic acid					
12 mole neopentyl glycol	25 g tributyl phosphate	141	14.1	415	15.6
13.2 mole C ₈ /C ₁₀ mono-basic acids					
6 mole adipic acid					
12 mole neopentyl glycol	25g tributyl phosphate	144	15.4	401	16.6
13.2 mole pelargonic acid					

COMPARATIVE TEST

As a comparison an ester was prepared using the same quantities and procedure as for the esters described in Example II, ex-

cept that 10g of paratoluene sulphonic acid were used in place of the phosphate. The oxidation resistance results were as follows:—

Oxidation Resistance of Ester in absence of antioxidants at 228°C.

After 20 hours		After 50 hours	
% increase	Δ Tan	% increase	Δ Tan
KV 210°F.	mg KOH/g	KV 210°C.	mg KOH/g
144	15.0	1050	22.1

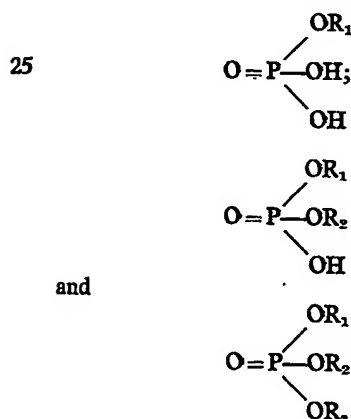
Thus, it can be clearly seen that the ester prepared using tributyl phosphate has superior oxidation stability to that prepared using only paratoluene sulphonic acid.

WHAT WE CLAIM IS:—

1. A process for preparing a complex ester (as hereinbefore defined) wherein the acidic and alcoholic reactants are reacted together in the presence of a phosphorus-containing compound (as hereinbefore defined).

2. A process as claimed in claim 1 wherein the phosphorus-containing compound is an ester of a phosphorus-containing acid.

3. A process as claimed in claim 2 wherein the ester is a partial or complete ester of phosphoric acid having the general formulae



wherein R_1 , R_2 and R_3 are similar or dissimilar hydrocarbyl groups.

4. A process as claimed in claim 3 wherein R_1 , R_2 and R_3 each contain between 1 and 10 carbon atoms.

5. A process as claimed in any one of the preceding claims wherein the phosphorus-containing compound is tributyl phosphate.

6. A process as claimed in any one of the preceding claims wherein less than 5% by weight of the reactants, of the phosphorus-containing compound is used.

7. A process as claimed in any one of the

preceding claims wherein an esterification catalyst is used.

8. A process as claimed in any one of the preceding claims wherein the reaction is carried out in two stages.

9. A process as claimed in claim 8 wherein the temperature of the first stage reaction is from 125°C to 175°C and the temperature of the second stage reaction is from 180°C to 220°C.

10. A process as claimed in any one of the preceding claims wherein the ester obtained is an acid-centered complex ester (as hereinbefore defined).

11. A process as claimed in any one of claims 1 to 9 wherein the ester obtained is a glycol-centered complex ester (as hereinbefore defined).

12. A process as claimed in any one of the preceding claims wherein the complex ester has a total of between 15 and 80 carbon atoms per molecule.

13. A process as claimed in any one of claims 1 to 10 and 12 wherein the ester is an acid-centered complex ester derived from adipic acid, neopentyl glycol and pelargonic acid.

14. A process as claimed in any one of claims 1 to 10 and 12 wherein the ester is an acid-centered complex ester derived from sebacic acid, neopentyl glycol and caprylic acid.

15. A process as claimed in any one of claims 1 to 10 and 12 wherein the ester is an acid-centered complex ester derived from sebacic acid, trimethylol propane and caprylic acid.

16. A process as claimed in any one of claims 1 to 11 wherein the ester is a glycol-centered complex ester derived from neopentyl glycol, sebacic acid and 2,2,4-trimethyl pentanol.

17. A process as claimed in any one of claims 1 to 11 wherein the ester is a glycol-centered complex ester derived from 2,2'-diethyl 1-3 propane diol, azelaic acid and 2,2,4-trimethyl pentanol.

18. A process substantially as hereinbefore

described with reference to either of the two
Examples.

19. A complex ester when prepared by a
process as claimed in any one of the preceding
5 claims.

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